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STATISTICS OF ONE-DIMENSIONAL CLUSTER MOTION.(U)

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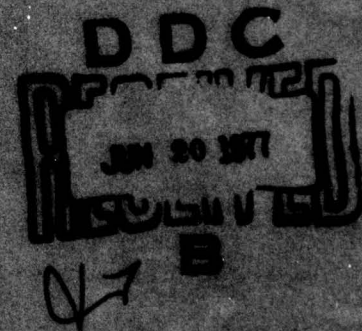
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STATISTICS OF ONE-DIMENSIONAL CLUSTER MOTION

JOHN D. WRIGLEY
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20. ABSTRACT (continued)

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→ diffusing on planes, such as W(211), on which nine distinct jump processes may contribute to the motion. In dimer diffusion, it is demonstrated that dissociation may be important even if the fraction dissociated is minor. For trimers, previous attempts to approximate the motion through the use of average transition rates are compared with the exact solutions and found wanting. Important statistical quantities beyond the mean square displacement are presented for simple dimers, capable of existing in only two states. The generating function is derived, together with the higher moments of the displacement. Probability density functions for the number of jumps in an interval t , for the waiting time up to a specified jump, as well as for the displacements, are all presented. These differ significantly from the density functions for an ordinary random walk. However, an averaging technique allows simple approximations for the behavior of dimers.

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by

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STATISTICS OF ONE-DIMENSIONAL CLUSTER MOTION*

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The statistics of clusters, made up of metal atoms in adjacent one-dimensional diffusion channels, are developed quantitatively. Kolmogorov's equation is used to find the mean square displacement for clusters capable of existing in energetically different configurations at the same displacement of the center of mass; this is done under steady state conditions, for which the probability of finding a specified configuration does not vary in time. Two systems are examined: (1) Dimers capable of existing in an infinite number of states, a situation realized if dissociation is allowed, and (2) Trimers diffusing on planes, such as W(211), on which nine distinct jump processes may contribute to the cluster motion. In dimer diffusion, it is demonstrated that dissociation may be important even if the fraction dissociated is minor. For trimers, previous attempts to approximate the motion through the use of average transition rates are compared with the exact solutions and found wanting. Important statistical quantities beyond the

mean square displacement are presented for simple dimers, capable of existing in only two states. The generating function is derived, together with the higher moments of the displacement. Probability density functions for the number of jumps in an interval t , for the waiting time up to a specified jump, as well as for the displacements, are all presented. These differ significantly from the density functions for an ordinary random walk. However, an averaging technique allows simple approximations for the behavior of dimers.

Quantitative observations of atomic clusters in the field ion microscope have recently made it possible to unravel the individual jump processes in the one-dimensional surface motion of dimers.¹ This analysis rests on a stochastic formalism for the diffusion process,² which relates the mean square displacement of the center of mass to the jump rates of the individual atoms in a cluster.³ Two simple statistical problems have so far been considered in detail: the mean square displacement of dimers, made up of atoms in adjacent diffusion channels and capable of existing in the two states labelled 0 and 1 in Fig. 1, and the diffusion of model trimers for which three jump rates suffice to describe the motion. Although the basis for an atomic analysis of cluster motion has been established, it still remains to elaborate the stochastic formalism and to cover the behavior of more complicated real systems. That is the present aim. We address ourselves to three related areas:

1. In the diffusion of dimers, dissociation into free atoms occasionally occurs at high temperatures.³ To assess the significance of these events in the analysis of dimer diffusion, the mean square displacement is evaluated for dimers that can exist in an infinity of different states.

2. The actual motion of trimers may depend upon nine different atomic steps.⁴ So far, this complicated motion has only been approximated. Here the diffusion of trimers will be examined in its generality, as a preliminary to the analysis of experimental observations, allowing all configurations that can be achieved by moving an atom one lattice spacing away from its neighbor.

3. Even for the motion of the simplest cluster, a non-dissociating dimer, only the mean square displacement has been worked out. For a proper understanding of cluster diffusion, as well as for assessing edge effects in real systems,⁵ the distribution governing the displacements of dimers must also be known. In the last section this distribution, together with other important statistical functions defining the random motion of dimers, is developed.

I. FORMALISM FOR CLUSTER DIFFUSION

In the previous discussion of cluster motion in one dimension,² only systems with a unique cluster configuration at each position of the center of mass were considered. This restriction is not inherent in the formalism, however, and can readily be removed to more adequately describe the actual surface motion of clusters. Throughout this presentation we still confine ourselves to clusters composed of atoms in adjacent diffusion channels, and moving in one dimension only, on a surface with spacing ℓ .

We proceed, just as in the past, to follow the migration of an m -mer by mapping the location of its center of mass on an infinite one-dimensional lattice, with spacing ℓ/m and m sites per unit cell. The random walk always begins in the unit cell based on $x=0$. Diffusion of this cluster is assumed to occur one atom jump at a time; regardless of the cluster configuration, each jump is presumed to span only a single surface spacing. In specifying the probability of finding a point x on the center of mass lattice occupied, it is now necessary to

explicitly recognize the existence of energetically different cluster configurations \underline{i} . The probability p_x that point x be occupied is now

$$p_x = \sum_i p_{x,i} \quad i = 0, 1, 2, \dots, \quad (1)$$

where the summation extends over all configurations \underline{i} accessible at x .

The transition rates from one site to the next also depend upon the configurations involved. A general formalism to handle this is outlined in the Appendix. Here it suffices to specify the rates starting from a given configuration \underline{i} , with $\lambda_{x,i}$ denoting the rate of transitions from x to $x+1$, and $\mu_{x,i}$ the rate from x to $x-1$. Kolmogorov's equation⁶ for the probability p_x therefore becomes

$$\frac{d}{dt} \sum_i p_{x,i} = \sum_i \lambda_{x-1,i} p_{x-1,i} - \sum_i (\lambda_{x,i} + \mu_{x,i}) p_{x,i} + \sum_i \mu_{x+1,i} p_{x+1,i} \quad (2)$$

With the additional definitions

$$\lambda_x p_x \equiv \sum_i \lambda_{x,i} p_{x,i} \quad \mu_x p_x \equiv \sum_i \mu_{x,i} p_{x,i} \quad (3)$$

equation (2) reduces to the usual form

$$\frac{dp_x}{dt} = \lambda_{x-1} p_{x-1} - (\lambda_x + \mu_x) p_x + \mu_{x+1} p_{x+1} \quad x = 0, \pm 1, \pm 2, \dots \quad (4)$$

The differential equation for $\langle (\Delta x)^2 \rangle$, the variance⁷ of x , follows just as previously

$$\frac{d\langle (\Delta x)^2 \rangle}{dt} = 2[\langle x \lambda_x \rangle - \langle x \mu_x \rangle - \langle x \rangle (\langle \lambda_x \rangle - \langle \mu_x \rangle)] + (\langle \lambda_x \rangle + \langle \mu_x \rangle) \quad (5)$$

However, the possibility of having i different cluster configurations, each with its own characteristic transition probabilities, at any point x , is now explicitly recognized by noting that

$$\begin{aligned}
 \langle \lambda_x \rangle &= \sum_x \sum_i \lambda_{x,i} p_{x,i} & \langle \mu_x \rangle &= \sum_x \sum_i \mu_{x,i} p_{x,i} \\
 \langle x \lambda_x \rangle &= \sum_x x \sum_i \lambda_{x,i} p_{x,i} & \langle x \mu_x \rangle &= \sum_x x \sum_i \mu_{x,i} p_{x,i} \\
 \langle x \rangle &= \sum_x x \sum_i p_{x,i}
 \end{aligned} \tag{6}$$

Although it appears that examination of cluster diffusion in terms of individual transition probabilities entails greater algebraic complexity when energetically different clusters are possible at a given site, the conceptual framework remains essentially the same as that already useful in earlier, simpler analyses. As specific examples of the application of Eq. (5) to cluster motion, we will analyze the linear diffusion of dimers as well as trimers. In experimental studies, the emphasis has been upon measurements under steady state conditions, such that the probability of observing different cluster configurations remains unchanging in time. In view of the complexity of the systems of interest, we shall throughout the first three sections limit ourselves to this steady state.

II. DIFFUSION OF DISSOCIATING DIMERS

A. Mean Square Displacements

In considering the coupled motion of two atoms in adjacent diffusion channels, it is expedient to label each energetically distinct dimer configuration by the separation of the two atoms, expressed in units of the surface spacing projected along the diffusion direction, as in Fig. 2. On an infinite lattice, an infinity of configurations is therefore possible on each site x . The finite range of interatomic forces insures that only a limited set of these configurations corresponds to bound pairs; the rest are independently migrating adatoms. This distinction will subsequently be of interest, but is not necessary at the moment - all configurations can be treated equivalently.

The rates important for dimer motion are designated according to the conventions illustrated in Fig. 2. Transitions for configuration \underline{i} to $\underline{i}+1$ are denoted by $\alpha_{\underline{i}}$, transitions from higher to lower configurations, that is, from \underline{i} to $\underline{i}-1$, by $\beta_{\underline{i}}$. The scheme of rate constants connecting various dimer configurations is shown in Fig. 3. Three features are important:

- 1) Even configurations appear on even sites of the center of mass lattice, odd configurations on odd sites.
- 2) Inasmuch as only single jumps are ever allowed, at most two rate constants enter into the movement of a given dimer configuration from one site to a neighbor.

Thus

$$\lambda_{x,i} = \mu_{x,i} = \alpha_{\underline{i}} + \beta_{\underline{i}}(1 - \delta_{i0}) , \quad (7)$$

where δ_{i0} is Kronecker's symbol. 3) The rate constants depend only upon the dimer configuration, and not explicitly upon the position x .

It is now an easy matter to evaluate the different contributions to Eq. (5). The rate constants averaged over position become

$$\begin{aligned}\langle \lambda_x \rangle &= \sum_x (\lambda_{x,0} p_{x,0} + \lambda_{x,1} p_{x,1} + \lambda_{x,2} p_{x,2} + \dots) \\ &= \sum_i [\alpha_i + \beta_i (1 - \delta_{i0})] p_i.\end{aligned}\quad (8)$$

Here we have adopted the notation

$$p_i \equiv \sum_x p_{x,i} \quad x = 0, \pm 1, \pm 2, \dots \quad (9)$$

to denote the probability of finding a specified configuration i , regardless of position on the center of mass lattice. The other terms appearing in Eq. (5) now follow immediately.

$$\langle \mu_x \rangle = \sum_i [\alpha_i + \beta_i (1 - \delta_{i0})] p_i = \langle \lambda_x \rangle \quad (10)$$

$$\begin{aligned}\langle x \lambda_x \rangle &= \sum_x x (\lambda_{x,0} p_{x,0} + \lambda_{x,1} p_{x,1} + \lambda_{x,2} p_{x,2} + \dots) \\ &= \alpha_0 \langle x \rangle_0 + (\alpha_1 + \beta_1) \langle x \rangle_1 + (\alpha_2 + \beta_2) \langle x \rangle_2 + \dots \\ &= \sum_i [\alpha_i + \beta_i (1 - \delta_{i0})] \langle x \rangle_i\end{aligned}\quad (11)$$

Here

$$\langle x \rangle_k = \sum_x x p_{x,k} \quad (12)$$

denotes the space average of x for a specified configuration k ; depending upon the parity of the configuration, this average will include either even or odd sites exclusively. Finally,

$$\langle x \mu_x \rangle = \sum_i [\alpha_i + \beta_i (1 - \delta_{i0})] \langle x \rangle_i = \langle x \lambda_x \rangle \quad (13)$$

Only two terms contribute to the differential equation for the variance of x , which now appears as

$$\frac{d\langle (\Delta x)^2 \rangle}{dt} = \langle \lambda_x \rangle + \langle \mu_x \rangle = 2 \sum_i [\alpha_i + \beta_i (1 - \delta_{i0})] P_i \quad (14)$$

We shall be concerned with the behavior of dimers over time intervals long enough for a steady state to be established; the terms $P_i = \sum_i p_{x,i}$ then no longer vary in time. Under these circumstances the requirements of detailed balance are satisfied if

$$\frac{P_1}{P_0} = \frac{\alpha_0}{\beta_1}, \quad \frac{P_2}{P_1} = \frac{\alpha_1}{\beta_2}, \quad \frac{P_{i+1}}{P_i} = \frac{\alpha_i}{\beta_{i+1}} \quad (15)$$

and

$$P_1 = \frac{\alpha_0}{\beta_1} P_0, \quad P_2 = \frac{\alpha_1}{\beta_2} P_1 = \frac{\alpha_0 \alpha_1}{\beta_1 \beta_2} P_0, \quad P_{i+1} = P_0 \prod_{j=0}^i \frac{\alpha_j}{\beta_{j+1}} \quad (16)$$

The normalization requirement

$$\sum_i P_i = 1 \quad (17)$$

now allows us to write

$$P_0 = \left(1 + \sum_i \prod_{j=0}^i \alpha_j / \beta_{j+1} \right)^{-1} \quad (18)$$

In the steady state, only constants appear on the right hand in Eq. (14). Furthermore, for the long time intervals characteristic of the steady state the precise starting point becomes unimportant. Equation (14) can now be integrated to give the variance of x :

$$\langle (\Delta x)^2 \rangle = 2t \sum_i [\alpha_i + \beta_i (1 - \delta_{i0})] P_i. \quad (19)$$

Using relations (16) and (18), this becomes

$$\begin{aligned} \langle (\Delta x)^2 \rangle &= 2t P_0 \alpha_0 [1 + (\alpha_1 + \beta_1)/\beta_1 + (\alpha_2 + \beta_2)\alpha_1/(\beta_1 \beta_2) + \dots] \\ &= 4t \alpha_0 \frac{(1 + \sum_{j=1}^i \prod \alpha_j / \beta_j)}{(1 + \sum_{j=0}^i \prod \alpha_j / \beta_{j+1})} \end{aligned} \quad (20)$$

We now have quite a general relation for the variance of the displacements executed by a dimer. This relation is capable of describing contributions from an unlimited number of different configurations,⁸ provided only that the transition rates α_i and β_i are all known. For our purposes, however, it is convenient to distinguish, somewhat artificially, between two types of configurations: those with i small, for which the two atoms of the dimer are bound to each other, and those with i large, for which atomic interactions have decayed to such an extent that the atoms move independently. Assume that the latter condition holds for $i \geq f$; then

$$\alpha_i = \beta_i = \alpha \quad i \geq f, \quad (21)$$

where α denotes half the total jump rate of a single atom. The factor of $1/2$ accounts for the fact that in the diffusion of single atoms, the total jump rate, rather than the rate in a specified direction, is traditionally specified. Equation (20) can now be written in the alternative form

$$\langle (\Delta x)^2 \rangle = 2t \left[\sum_{i=0}^{f-1} [\alpha_i + \beta_i (1 - \delta_{i0})] P_i + 2\alpha P_s \right], \quad (22)$$

where

$$P_s \equiv \sum_{i \geq f} P_i \quad (23)$$

denotes the probability of finding a free dimer.

B. Specific Examples

In the limit $P_s=1$, that is as dissociated dimers dominate, the variance of the displacements, Eq. (22), becomes

$$\langle (\Delta x)^2 \rangle = 4\alpha t. \quad (24)$$

This describes the movement of two free atoms on the center of mass lattice, with a grid spacing of $\ell/2$. For free atoms, an expression for $\langle (\Delta x)^2 \rangle$ can be obtained independently of the preceding. The coordinate x of the center of mass is related to the coordinates y_1 and y_2 of the 2 atoms on the real lattice by

$$x = y_1 + y_2. \quad (25)$$

It therefore follows that

$$\langle (\Delta x)^2 \rangle = \langle (\Delta y_1)^2 \rangle + \langle (\Delta y_2)^2 \rangle + 2 \langle \Delta y_1 \Delta y_2 \rangle. \quad (26)$$

If the movements of the atoms are uncorrelated, then

$$\langle (\Delta x)^2 \rangle = 2 \langle (\Delta y)^2 \rangle \quad . \quad (27)$$

For the random walk of a single atom,⁶ however, we have

$$\langle (\Delta y)^2 \rangle = 2 \alpha t \quad , \quad (28)$$

yielding for $\langle (\Delta x)^2 \rangle$, the variance of the center of mass coordinate, exactly the same expression as derived from our general formalism for pairs.

If dissociation is unimportant, so that $P_g=0$ and only the two bound states 0 and 1 are possible, then $\alpha_1=0$ and Eq. (22) transforms to

$$\langle (\Delta x)^2 \rangle = 4\alpha_0 \beta_1 t / (\alpha_0 + \beta_1) \quad , \quad (29)$$

the relation already derived in I. This model appears to describe the available data for dimers on the (211) plane of tungsten. However, in quantitative studies by Stolt et al.,³ the dimers were observed to dissociate occasionally. In order to estimate the effects of such events, we assume that dimers in configuration $i \geq 3$ are entirely free and that atomic interactions have ceased to be important once the interatomic separation amounts to $2l$. This situation is indicated schematically by the potential diagram in Fig. 4. The transition rate α_2 is then just equal to the rate α in the free dimer,

$$\alpha = \nu_\alpha \exp - \Delta E_\alpha^\ddagger / kT, \quad (30)$$

where ΔE_α^\ddagger is the activation energy and ν_α the prefactor for jumping.

The variance of x now becomes

$$\langle (\Delta x)^2 \rangle = 4tP_1\{\beta_1 + \alpha_1 + \alpha[P_2/(2P_1) + P_s/P_1]\} . \quad (31)$$

The probability ratios P_2/P_1 and P_s/P_1 depend only upon the thermodynamics of the different dimer configurations and in principle are accessible to direct observation. The rate α is available from separate measurements on the diffusion of single atoms. This still leaves the two transition rates β_1 and α_1 , with only Eq. (31) to connect them to experiment. However, the rate α_1 at which dimers change from configuration 1 to 2 is fixed within limits by the ratio P_2/P_1 , that is, by the thermodynamics of configuration 2 relative to 1. In the worst case, we are likely to have

$$\alpha_1 = \nu_{\alpha_1} \exp - \Delta E_{\alpha_1}^\ddagger / kT, \quad (32)$$

with $\nu_{\alpha_1} \sim \nu_\alpha$, $\Delta E_{\alpha_1}^\ddagger = \Delta E_\alpha^\ddagger$; a more likely event is that

$$\Delta E_{\alpha_1}^\ddagger \sim \Delta E_\alpha^\ddagger + cE_2 \quad 0 < c \leq 1, \quad (33)$$

where E_2 stands for the energy of configuration 2 relative to that of configuration 1.

Numerical estimates for the effects of dissociation upon the mean square displacement are shown in Fig. 5 for a system modeled on the behavior of rhenium dimers on W(211).³ It appears that dissociation can significantly affect the mean square displacements. If a sizeable fraction of the dimers can transgress beyond the 0 and 1 configurations,

then $\langle (\Delta x)^2 \rangle$ diminishes, as the mobility of free atoms in this model system is less than that of bound dimers. It is obvious that these effects must be allowed for in the analysis of experimental observations.

The corrections for dissociation do not sensitively depend upon the particular assumptions concerning α_1 , the unknown rate of transition from configuration 1 to 2. Even in the unlikely worst case, the variance of x differs only by $\approx 10\%$ from that found with the more likely smaller values of α_1 , for which the actual magnitude of the rate has hardly any effect on $\langle (\Delta x)^2 \rangle$. It is of interest that the dependence of the variance upon the particular assumptions concerning α_1 is greatest when the fraction of dimers in state 2 is least. In principle, it is possible to have an entirely negligible amount of dissociation and yet have important contributions to the diffusion from configurations such as 2. Physically this happens if transitions from configuration 1 to 2 are possible, but the return rate is much faster. No appreciable concentration can build up in state 2; every time a transition into this configuration occurs, it is immediately followed by the reverse process. However, each of these events means a displacement of the dimer above and beyond that of a dimer with only two allowed configurations.

It is important to consider this possibility in interpreting the diffusion of dimers. Even if no dissociation is actually observed in an experiment, the analysis should properly be carried out with a model incorporating the effects of dissociating dimers. This can be accomplished using the thermodynamic information to guess at the value of the transition rate from configuration 1 to 2, and estimating the jump rates with and without allowing dissociation.

III. TRIMER DIFFUSION

The linear migration of trimers can be handled in much the same way as that of dimers, although the nomenclature becomes more complicated. The unit cell of the lattice on which motion of the center of mass is mapped now contains three points; as shown in Fig. 6, two energetically different trimer configurations are possible at each such point. The convention found useful in designating dimer configurations in Sec. II no longer suffices for trimers. We therefore retain the labelling devised in I. In this scheme, slanted or V shaped configurations are distinguished from the others by adding B or A respectively to the usual configuration index.⁹ The different terms entering Eq. (5) for the variance of x can now be readily evaluated. Keeping in mind that trimer configuration 0 occurs only on sites of type 0, configuration 1 on sites of type 1, etc., it immediately follows that

$$\begin{aligned} \langle \lambda_x \rangle = & (a_I + a_{II}) \Sigma_0 p_{x,0A} + a_{III} \Sigma_0 p_{x,0B} \\ & + (b_I + b_{II}) \Sigma_1 p_{x,1A} + b_{III} \Sigma_1 p_{x,1B} + (c_I + c_{II}) \Sigma_2 p_{x,2A} \\ & + c_{III} \Sigma_2 p_{x,2B} ; \end{aligned} \quad (34)$$

symbols such as Σ_1 , for example, indicate summation over x for all sites of type 1. The averaged transition rate $\langle \lambda_x \rangle$ can be written more compactly as

$$\begin{aligned} \langle \lambda_x \rangle = & (a_I + a_{II}) P_{0A} + (b_I + b_{II}) P_{1A} + (c_I + c_{II}) P_{2A} \\ & + a_{III} P_{0B} + b_{III} P_{1B} + c_{III} P_{2B} , \end{aligned} \quad (35)$$

where, in conformity with the conventions for dimers, we use the

abbreviation

$$P_{OA} \equiv \sum_x P_{x,OA} \quad (36)$$

to describe the probability of finding a configuration, such as OA in this instance, regardless of position x . We recall² that under steady state conditions these probabilities are connected by a number of simplifying relations:

$$\begin{aligned} P_{1A} &= P_{2A} & P_{1B} &= P_{2B} \\ P_{1A} &= P_{OA} a_I / c_I & P_{1B} &= P_{OA} a_{II} / c_{III} \\ P_{OB} &= P_{OA} a_I c_{II} / (c_I a_{III}) \\ P_{OA} &= [1 + 2a_I / c_I + 2a_{II} / c_{III} + a_I c_{II} / (c_I a_{III})]^{-1} . \end{aligned} \quad (37)$$

Equation (35) therefore simplifies to

$$\begin{aligned} \langle \lambda_x \rangle &= (a_I + a_{II})P_{OA} + (b_I + b_{II} + c_I + c_{II})P_{1A} \\ &\quad + a_{III}P_{OB} + (b_{III} + c_{III})P_{1B} . \end{aligned} \quad (38)$$

Similarly,

$$\begin{aligned} \langle \mu_x \rangle &= (a_I + a_{II})P_{OA} + (b_I + b_{II} + c_I + c_{II})P_{1A} \\ &\quad + a_{III}P_{OB} + (b_{III} + c_{III})P_{1B} = \langle \lambda_x \rangle , \end{aligned} \quad (39)$$

$$\begin{aligned} \langle x \lambda_x \rangle &= \sum_x x [(a_I + a_{II})P_{x,OA} + a_{III}P_{x,OB} + (b_I + b_{II})P_{x,1A} \\ &\quad + b_{III}P_{x,1B} + (c_I + c_{II})P_{x,2A} + c_{III}P_{x,2B}] \\ &= (a_I a_{II}) \langle x \rangle_{OA} + (b_I + b_{II}) \langle x \rangle_{1A} + (c_I + c_{II}) \langle x \rangle_{2A} \\ &\quad + a_{III} \langle x \rangle_{OB} + b_{III} \langle x \rangle_{1B} + c_{III} \langle x \rangle_{2B} . \end{aligned} \quad (40)$$

Here we have resorted to the convention

$$\langle x \rangle_{1A} \equiv \sum_1 x p_{x,1A} \quad (41)$$

to indicate the average of x for a specific trimer configuration, in this instance 1A. The last remaining term in Eq. (5) is

$$\begin{aligned} \langle x_{1A} \rangle = & (a_I + a_{II}) \langle x \rangle_{0A} + (c_I + c_{II}) \langle x \rangle_{1A} + (b_I + b_{II}) \langle x \rangle_{2A} + a_{III} \langle x \rangle_{0B} \\ & + c_{III} \langle x \rangle_{1B} + b_{III} \langle x \rangle_{2B} \end{aligned} \quad (42)$$

The differential equation for the variance of x can now be written as

$$\begin{aligned} \frac{d\langle (\Delta x)^2 \rangle}{dt} = & 2\{ (b_I - c_I + b_{II} - c_{II}) (\langle x \rangle_{1A} - \langle x \rangle_{2A}) + (b_{III} - c_{III}) (\langle x \rangle_{1B} - \langle x \rangle_{2B}) \\ & + P_{0A} [2(a_I + a_{II}) + (b_I + 2b_{II} + 2c_{II}) a_I / c_I] \} \end{aligned} \quad (43)$$

We still require the two terms

$$X_A \equiv \langle x \rangle_{1A} - \langle x \rangle_{2A}, \quad X_B \equiv \langle x \rangle_{1B} - \langle x \rangle_{2B} \quad (44)$$

To derive these we need the probability $p_{x,i}$ of having a specified configuration at the point x . This can be obtained from Kolmogorov's equation, as shown in the Appendix. For $p_{x,1A}$ as an example, the appropriate differential expression is

$$\begin{aligned} \frac{dp_{x,1A}}{dt} = & a_I p_{x-1,0A} + a_{III} p_{x-1,0B} - (b_I + b_{II} + c_I + c_{II}) p_{x,1A} \\ & + b_I p_{x+1,2A} + b_{III} p_{x+1,2B} \end{aligned} \quad (45)$$

It follows in the usual way that

$$\begin{aligned} \frac{d\langle x \rangle_{1A}}{dt} = & a_I (\langle x \rangle_{0A} + P_{0A}) - (b_I + c_I + b_{II} + c_{II}) \langle x \rangle_{1A} \\ & + b_I (\langle x \rangle_{2A} - P_{2A}) + a_{III} (\langle x \rangle_{0B} + P_{0B}) + b_{III} (\langle x \rangle_{2B} - P_{2B}) . \end{aligned} \quad (46)$$

In much the same fashion, it can be shown that

$$\begin{aligned} \frac{d\langle x \rangle_{2A}}{dt} = & b_I (\langle x \rangle_{1A} + P_{1A}) - (b_I + c_I + b_{II} + c_{II}) \langle x \rangle_{2A} \\ & + a_I (\langle x \rangle_{0A} - P_{0A}) + a_{III} (\langle x \rangle_{0B} - P_{0B}) + b_{III} (\langle x \rangle_{1B} + P_{1B}) . \end{aligned} \quad (47)$$

Using the steady state relations (37) and the definitions of Eq. (44), we find

$$\frac{dX_A}{dt} = - (2b_I + c_I + b_{II} + c_{II}) X_A - b_{III} X_B - 2(b_I - c_I + b_{II} - c_{II}) P_{0A} a_I / c_I . \quad (48)$$

The differential equation for X_B follows from an analogous sequence of steps as

$$\frac{dX_B}{dt} = - (b_{III} + c_{III}) X_B - b_{II} X_A - 2(b_{II} a_I / c_I - a_{II}) P_{0A} . \quad (49)$$

Only the steady state, in which the time dependence becomes unimportant, is of interest. Equations (48) and (49) therefore reduce to

$$\begin{aligned} (2b_I + c_I + b_{II} + c_{II}) X_A + b_{III} X_B &= - 2(b_I - c_I + b_{II} - c_{II}) P_{0A} a_I / c_I \\ b_{II} X_A + (b_{III} + c_{III}) X_B &= - 2(b_{II} a_I / c_I - a_{II}) P_{0A} , \end{aligned} \quad (50)$$

with the solution

$$X_A = 2P_{0A} \frac{a_I \Delta_A}{c_I \Delta} \quad X_B = 2P_{0A} \frac{a_I \Delta_B}{c_I \Delta} \quad (51)$$

$$\Delta_A \equiv [b_{III} (b_{II} - a_{II} c_I / a_I) - (b_I - c_I + b_{II} - c_{II}) (b_{III} + c_{III})]$$

$$\Delta_B \equiv [b_{II} (b_I - c_I + b_{II} - c_{II}) - (b_{II} - a_{II} c_I / a_I) (2b_I + c_I + b_{II} + c_{II})]$$

$$\Delta \equiv (2b_I + c_I + b_{II} + c_{II})(b_{III} + c_{III}) - b_{II}b_{III}.$$

Substituting these results in Eq. (43) and integrating, the variance of the center of mass displacements for trimers appears as

$$\begin{aligned} \langle (\Delta x)^2 \rangle = 4tP_{0A} [& (b_I - c_I + b_{II} - c_{II})\Delta_A/\Delta + (b_{III} - c_{III})\Delta_B/\Delta \\ & + c_I(1 + a_{II}/a_I) + (b_I + 2b_{II} + 2c_{II})/2] a_I/c_I. \end{aligned} \quad (52)$$

In the limit as $a_{II} = b_{II} = c_{II} = 0$, trimer migration can only proceed through A configurations. This possibility has been treated exactly in I. For such a diffusion path, Eq. (52) simplifies to

$$\langle (\Delta x)^2 \rangle = \frac{18 a_I b_I c_I t}{(2a_I + c_I)(2b_I + c_I)}, \quad (53)$$

which is precisely the relation previously derived. If the transition rates meet the condition $b_{II} = c_I = 0$, then diffusion must occur by movement of the trimer through the configurations 0B, 1A, and 2A only. This constitutes another symmetrical path, for which Eq. (52) yields

$$\langle (\Delta x)^2 \rangle = \frac{18 a_{III} b_I c_{II} t}{(2a_{III} + c_{II})(2b_I + c_{II})}, \quad (54)$$

again in agreement with previous work.

The complete equation for trimer diffusion involves nine transition rates.⁴ These are not all accessible to direct observation in any straightforward way, but Eq. (52) makes it feasible to model the behavior of trimers for a known interatomic force law. An approximate procedure has been suggested in the past.² In this the motion is idealized as occurring via a symmetric path through the unit cell; average rate constants are

then used to account for the presence of energetically different configurations at a lattice point. Tests with model potentials reveal that this approximation works surprisingly well in many instances, yielding mean square displacements within 25% of the true values. Under these circumstances the diffusion parameters deduced from the usual Arrhenius plots are essentially without error. However, for some combinations of physically reasonable rate constants the average rate approximation fails by more than an order of magnitude. Despite its complexity, the exact relation (52) for the variance of the center of mass positions must therefore be used in modeling the diffusion of trimers.

IV. STATISTICS OF TWO-STATE DIMERS

The emphasis up to this point has been upon the mean square displacements executed by the center of mass of a cluster during surface diffusion. The distribution of displacements, as well as higher moments of the distribution, are also of concern. From a practical point of view, we note that one-dimensional diffusion is observed on planes of finite size, so that corrections have to be made for the possible effects of the edges. The simple relations available for this, however, are based on the assumption, as yet not tested, that the displacements can be approximated by a Gaussian distribution. More than that, the one-dimensional motion of clusters also constitutes a novel type of random walk, of interest in its own right. Here we therefore derive several statistical quantities important in describing cluster motion.

We confine ourselves to the simplest clusters, to dimers that can only exist in the two configurations 0 and 1 indicated schematically in Fig. 1. Transitions from $x=0$ to $x=1$ are assumed to occur at the rate \underline{a} , from $x=1$ to $x=0$ at the rate \underline{b} . That is, in the general scheme indicated in Fig. 2, $\alpha_0 = \underline{a}$ and $\beta_1 = \underline{b}$; all other rates vanish. To ease the derivation of higher moments, which in principle are directly accessible through Kolmogorov's equation, we first develop the probability generating function $G(z)$, defined by

$$G(z) \equiv \sum_x z^x p_x \quad x = 0, \pm 1, \pm 2, \dots \quad (55)$$

The distribution governing dimer displacements is presented separately. Also of interest for characterizing the random walk of dimers is the probability density function for the total number of jumps, and for the time required to make a fixed number of jumps, the first of which plays a key role in the distribution of displacements. In the last section, both are derived and compared with the behavior of simple random walks.

A. Generating Function and Moments

Starting from Kolmogorov's relation, Eq. (4), it follows quite generally that

$$\frac{\partial G(z)}{\partial t} = \sum_x z^x \lambda_{x-1} p_{x-1} - \sum_x z^x (\lambda_x + \mu_x) p_x + \sum_x z^x \lambda_{x+1} p_{x+1} \quad (56)$$

For dimers, this differential equation reduces to

$$\dot{G}(z) = (u - 2)(aG_0 + bG_1), \quad (57)$$

where $\dot{G}(z)$ denotes the time derivative of the generating function and we have introduced the definitions

$$\begin{aligned} u &\equiv z + 1/z \\ G_0 &\equiv \sum_0 z^x p_x \\ G_1 &\equiv \sum_1 z^x p_x \end{aligned} \quad (58)$$

To proceed further, the sums G_0 and G_1 over even and odd sites, respectively, must be expressed in terms of the dimer transition rates. Again from Kolomogorov's relation, we find the coupled differential equations

$$\begin{aligned}\dot{G}_0 &= buG_1 - 2aG_0 \\ \dot{G}_1 &= auG_0 - 2bG_1\end{aligned}\quad (59)$$

Laplace transformation converts these into the form

$$\begin{aligned}(s + 2a)\mathcal{L}\{G_0\} - bu\mathcal{L}\{G_1\} &= G_0[t=0] \\ - au\mathcal{L}\{G_0\} + (s + 2b)\mathcal{L}\{G_1\} &= G_1[t=0]\end{aligned}\quad ;\quad (60)$$

s is as usual the argument of the Laplace transform, and the values of G_0 and G_1 at time $t=0$ are denoted by $G_0[t=0]$ and $G_1[t=0]$ respectively. For excursions starting from even sites,¹⁰

$$G_0^{(0)}[t=0] = 1, \quad G_1^{(0)}[t=0] = 0, \quad (61)$$

for excursions from odd sites,

$$G_0^{(1)}[t=0] = 0, \quad G_1^{(1)}[t=0] = z; \quad (62)$$

the origin of the dimers is indicated explicitly by the appropriate superscript. For the moment confining ourselves to excursions starting at an even site, we find

$$\mathcal{L}\{G_0^{(0)}\} = \frac{s + 2b}{(s + q)(s + r)} \quad (63)$$

$$\mathcal{L}\{G_1^{(0)}\} = \frac{au}{(s + q)(s + r)},$$

where

$$\begin{aligned}
 q &\equiv (a+b)\{1 + [1 + ab(u^2 - 4)/(a+b)^2]^{\frac{1}{2}}\} \\
 r &\equiv (a+b)\{1 - [1 + ab(u^2 - 4)/(a+b)^2]^{\frac{1}{2}}\} .
 \end{aligned}
 \tag{64}$$

The inverse transformation¹¹ of Eq. (63) yields the desired quantities

$$\begin{aligned}
 G_0^{(0)} &= \frac{(q-2b)}{(q-r)} \exp(-qt) - \frac{(r-2b)}{(q-r)} \exp(-rt) \\
 G_1^{(0)} &= -\frac{au}{(q-r)} [\exp(-qt) - \exp(-rt)] .
 \end{aligned}
 \tag{65}$$

Substituting these in Eq. (57) and integrating gives the generating function $G^{(0)}(z)$ for starts at even sites as

$$\begin{aligned}
 G^{(0)}(z) &= 1 + \frac{a(u-2)}{(q-r)} \{ [q-b(u+2)][1-\exp(-qt)]/q \\
 &\quad - [r-b(u+2)][1-\exp(-rt)]/r \} .
 \end{aligned}
 \tag{66}$$

A similar sequence of steps yields the generating function $G^{(1)}(z)$ for excursions from odd sites:

$$\begin{aligned}
 G^{(1)}(z) &= z + \frac{zb(u-2)}{(q-r)} \{ [q-a(u+2)][1-\exp(-qt)]/q \\
 &\quad - [r-a(u+2)][1-\exp(-rt)]/r \} .
 \end{aligned}
 \tag{67}$$

In the limit as the transition rates \underline{a} and \underline{b} become equal, the generating function for starts at x_0 reduces to

$$G^{(x_0)}(z) = z^{x_0} \exp a(u-2)t \quad a=b, \tag{68}$$

appropriate for a simple random walk over discrete sites but continuous in time.

The n^{th} moment $\langle x^n \rangle$ of the coordinate of the center of mass is now easily accessible,⁶ through repeated differentiation of the generating function according to

$$\left(z \frac{\partial}{\partial z} \right)^n G(z) \Big|_{z=1} = \sum_x x^n p_x = \langle x^n \rangle. \quad (69)$$

We display only the 2nd and 4th moments; the odd moments vanish for excursions starting from even sites.

$$\langle x^2 \rangle(0) = \frac{2a}{a+b} \left\{ 2bt + \frac{(a-b)}{2(a+b)} [1 - \exp(-2(a+b)t)] \right\} \quad (70)$$

$$\langle x^2 \rangle(1) = 1 + \frac{2b}{a+b} \left\{ 2at - \frac{(a-b)}{2(a+b)} [1 - \exp(-2(a+b)t)] \right\}$$

$$\begin{aligned} \langle x^4 \rangle(0) = & \frac{8ab}{(a+b)^2} \left\{ 6abt^2 + 3at \frac{(a-b)}{(a+b)} \exp(-2(a+b)t) \right. \\ & \left. + \frac{(5a^2 - 5ab + 2b^2)t}{(a+b)} + \frac{(a-b)(a^2 - 28ab + 7b^2)}{8b(a+b)^2} [1 - \exp(-2(a+b)t)] \right\} \end{aligned} \quad (71)$$

$$\begin{aligned} \langle x^4 \rangle(1) = & 1 + \frac{8ab}{(a+b)^2} \left\{ 6abt^2 - 3bt \frac{(a-b)}{(a+b)} \exp(-2(a+b)t) \right. \\ & \left. + \frac{(5a^2 + ab + 8b^2)t}{(a+b)} - \frac{(a-b)(13a^2 - 16ab + 7b^2)}{8a(a+b)^2} [1 - \exp(-2(a+b)t)] \right\}. \end{aligned}$$

In the limit $a=b$, the moments simplify to

$$\begin{aligned} \langle x^2 \rangle(0) &= 2at \\ \langle x^2 \rangle(1) &= 2at + 1 \end{aligned} \quad (72)$$

$$\begin{aligned} \langle x^4 \rangle(0) &= 12a^2 t^2 + 2at \\ \langle x^4 \rangle(1) &= 1 + 12a^2 t^2 + 14at \end{aligned} \quad (73)$$

These are precisely the values for an ordinary random walk in continuous time.

For a Gaussian walk characterized by a total jump rate 2λ and starting at the origin,

$$\begin{aligned}\langle x^4 \rangle &= 3 \langle x^2 \rangle^2 \\ \langle x^2 \rangle &= 2\lambda t\end{aligned}\tag{74}$$

We note that in the limit of long times, only the first term in braces occurring in Eqs. (70) and (71) contributes. In this limit, therefore, the ratio of the 4th to the 2nd moment for dimer displacements is exactly that for a Gaussian walk. The 2nd moment for dimers is, of course, equal to that of a Gaussian, but with an effective jump rate $\lambda = 2ab/(a+b)$. In short, for the lower moments at least, a Gaussian approximation is appropriate.

B. Probability Densities

1. General Approach

In principle the distribution governing cluster displacements can be obtained from the generating function $G(z)$ by expansion in a Laurent series. We adopt a simpler, physically more transparent approach.

For the center of mass to end at point x after N jumps, having started at x_0 , it must take $[N + (x - x_0)]/2$ steps to the right and $[N - (x - x_0)]/2$ to the left; jumps to the right and to the left are assumed equally probable. The conditional probability $f\{x|N\}$ of ending at x , given a total of N jumps, therefore obeys the binomial law⁶

$$f\{x|N\} = \binom{N}{\frac{N+x-x_0}{2}} 2^{-N};\tag{75}$$

note that $f\{x|N\} = 0$ if N and $(x - x_0)$ are not of the same parity. The joint probability $f\{x, N\}$ of the center of mass being at x after N jumps is

$$f\{x, N\} = p_N(t) f\{x|N\} \quad , \quad (76)$$

where $p_N(t)$ denotes the probability that during an interval t a dimer will make a total of N jumps.

To obtain the desired probability p_x of a dimer ending at x , we just sum¹² over all jumps N

$$p_x = \sum_{N=0}^{\infty} p_N(t) f\{x|N\} \quad . \quad (77)$$

It now remains to derive the probability density $p_N(t)$ describing the total number of jumps executed by the center of mass during time t . Closely connected to the number of jumps during such an interval is the time T_k required to make a fixed number, k , of jumps. Although not directly involved in arriving at p_x , the time distribution is of interest in characterizing those aspects of the motion of dimers distinct from ordinary random walks. The probability densities for N and for T_k are therefore derived separately in the next two sections.

2. Probability Density for the Number of Jumps N

We seek the probability $p_N(t)$ that, as the dimer moves along the lattice, it will make a total of N jumps in the time interval t . Let λ_N denote the rate of making the $(N+1)^{th}$ jump. Inasmuch as the number of jumps N can never decrease, Kolmogorov's equation for $p_N(t)$ becomes¹³

$$\frac{dp_0(t)}{dt} = -\lambda_0 p_0(t) \quad (78)$$

$$\frac{dp_N(t)}{dt} = \lambda_{N-1} p_{N-1}(t) - \lambda_N p_N(t) \quad N > 0. \quad (79)$$

The Laplace transforms of $p_N(t)$ are therefore

$$\mathcal{L}\{p_0(t)\} = \frac{1}{s + \lambda_0} \quad (80)$$

$$\mathcal{L}\{p_N(t)\} = \frac{\lambda_{N-1}}{s + \lambda_N} \mathcal{L}\{p_{N-1}(t)\} \quad N > 0. \quad (81)$$

Equations (80) and (81) immediately lead to the general relation

$$\mathcal{L}\{p_N(t)\} = \frac{1}{s + \lambda_0} \prod_{j=0}^{N-1} \frac{\lambda_j}{s + \lambda_{j+1}} \quad N > 0. \quad (82)$$

If excursions start at an even site, then the rate of jumping for dimers is given by

$$\begin{aligned} \lambda_N &= 2a & N \text{ even} \\ \lambda_N &= 2b & N \text{ odd} \end{aligned} \quad (83)$$

We shall only present solutions for this situation, but note that for excursions starting at an odd site, a and b are interchanged throughout. With the rates defined by (83),

$$\mathcal{L}\{p_N^{(0)}(t)\} = \frac{(2a)^{N/2} (2b)^{N/2}}{(s+2a)^{(N+2)/2} (s+2b)^{N/2}} \quad N \text{ even} \quad (84)$$

$$\mathcal{L}\{p_N^{(0)}(t)\} = \frac{(2a)^{(N+1)/2} (2b)^{(N-1)/2}}{(s+2a)^{(N+1)/2} (s+2b)^{(N+1)/2}} \quad N \text{ odd} \quad (85)$$

For an odd number of jumps the inverse transform is immediately available, and gives

$$p_N^{(0)}(t) = \frac{(2a)^{(N+1)/2} (2b)^{(N-1)/2}}{\left(\frac{N-1}{2}\right)!} \frac{\prod_{j=0}^{N/2} t^{N/2} \exp[-(a+b)t]}{[2(a-b)]^{N/2}} I_{N/2}[(a-b)t] \quad (86)$$

$N \text{ odd}.$

The solution for an even number of jumps is obtained, by substituting (86) in Eq. (79) and integrating, as

$$p_N^{(0)}(t) = \frac{(2a)^{N/2} (2b)^{N/2}}{2(N/2)!} \Pi_{\frac{1}{2}}^{(N+1)/2} \frac{\exp[-(a+b)t]}{[2(a-b)]^{(N-1)/2}} \{ I_{(N-1)/2}^{[(a-b)t]} - I_{(N+1)/2}^{[(a-b)t]} \} \quad N \text{ even} \quad (87)$$

Here $I_{n+\frac{1}{2}}(z)$ is the modified spherical Bessel function of the first kind. As the rates \underline{a} and \underline{b} approach each other, dimer behavior becomes independent of site, and the total number of jumps should therefore conform⁶ to a Poisson distribution. The limiting form of $p_N(t)$ when $\underline{a} = \underline{b}$ can be obtained making use of the series¹¹

$$\sqrt{\frac{\pi}{2z}} I_{n+\frac{1}{2}} = \frac{z^n}{1 \cdot 3 \cdot 5 \dots (2n+1)} \left\{ 1 + \frac{z^2/2}{1!(2n+3)} + \frac{(z^2/2)^2}{2!(2n+3)(2n+5)} + \dots \right\} \quad (88)$$

and the identity

$$1 \cdot 3 \cdot 5 \dots (2k-1) \cdot (2^k k!) = (2k)! \quad (89)$$

Both Eq. (86) and (87) reduce to the proper form

$$p_N(t) = \frac{(2at)^N \exp - 2at}{N!} \quad (90)$$

The probability density for the number of jumps by a dimer is compared in Fig. 7 with the behavior typical of an ordinary random walk, for which the jump rates are independent of position, and $\underline{a} = \underline{b}$. As expected, when the jump rates differ significantly, there are pronounced variations in the probability density on going from an odd to an even number of jumps.

In Fig. 8, the average of the probabilities for two neighboring jumps, when the rates \underline{a} and \underline{b} are significantly different, is compared with the same average for a Poisson distribution, characteristic of an ordinary random walk. The agreement is quite reasonable. Averaging over adjacent values of N eliminates the large excursions in the probability, revealing overall trends for dimers which are quite similar to those in a simple random walk.

3. Probability Density for the Waiting Time T_k

Basic to the development in this section has been the assumption that cluster diffusion can be described as occurring via atomic jumps random in time, with transition rates depending only upon the state of the system from which the jump takes place. That is, the elapsed time τ_i between jumps \underline{i} and $\underline{i} + 1$ has an exponential probability density

$$f_i(\tau) = \lambda_i \exp - \lambda_i \tau, \quad (91)$$

where λ_i denotes the rate of the $(i+1)^{th}$ jump. The time T_k at which the k^{th} jump takes place is given by the sum

$$T_k = \sum_{i=0}^{k-1} \tau_i. \quad (92)$$

The waiting times τ_i for individual jumps are independent quantities, each with a characteristic function

$$\phi_i(\theta) \equiv \int_{-\infty}^{\infty} \exp(j\theta\tau) f_i(\tau) d\tau = \frac{\lambda_i}{\lambda_i - j\theta}, \quad (93)$$

where $j^2 = -1$. Because of this independence, the characteristic function $\phi_{T_k}(\theta)$ for the probability density of T_k is⁶

$$\phi_{T_k}(\theta) = \prod_{i=0}^{k-1} \phi_i(\theta) = \prod_{i=0}^{k-1} \frac{\lambda_i}{\lambda_i - j\theta} \quad (94)$$

Substituting the jump rates (83) appropriate to dimers, the characteristic function of T_k for excursions starting at an even site is found as

$$\phi_{T_k}^{(0)}(\theta) = [2a/(2a-j\theta)]^{(k+1)/2} [2b/(2b-j\theta)]^{(k-1)/2} \quad k \text{ odd} \quad (95)$$

$$\phi_{T_k}(\theta) = [2a/(2a-j\theta)]^{k/2} [2b/(2b-j\theta)]^{k/2} \quad k \text{ even.}$$

For excursions from odd sites, a and b must be interchanged. The desired probability density function $f_{T_k}(t)$ is now obtained from the exponential Fourier transform¹⁴ of $\phi_{T_k}(\theta)$,

$$f_{T_k}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-j\theta t) \phi_{T_k}(\theta) d\theta \quad (96)$$

as

$$\begin{aligned} f_{T_k}^{(0)}(t) &= (2a)^{(k+1)/2} (2b)^{(k-1)/2} \exp(-2at) \\ &\times [t^{k-1}/(k-1)!] {}_1F_1[(k-1)/2; k; (2a-2b)t] \quad k \text{ odd} \\ f_{T_k}(t) &= (2a)^{k/2} (2b)^{k/2} \exp(-2at) [t^{k-1}/(k-1)!] {}_1F_1[k/2; k; (2a-2b)t] \quad k \text{ even.} \end{aligned} \quad (97)$$

Here ${}_1F_1(a; c; z)$ denotes Kummer's confluent hypergeometric series.

In the limit as $a=b$, jumping becomes a Poisson process, in which the waiting time for the k^{th} jump is known to conform to a gamma distribution.⁶

Also in this limit, the Kummer functions in Eq. (97)

approach unity. The probability density for the time at which the k^{th} jump occurs then is

$$f_{T_k}(t) = (2a)^k [t^{k-1}/(k-1)!] \exp - 2at \quad (98)$$

As expected, this is just the gamma distribution of order k .

Probability densities according to Eq. (97) are plotted in Fig. 9. In these graphs, the probabilities calculated for different values of the rates a and b are compared with each other, always keeping $\lambda = 2ab/(a+b)$ constant. When the number of jumps k is small, different choices of a and b yield significantly different curves. Of course for k even, the plots are invariant to an interchange of a and b . Despite that, the probabilities for $a \neq b$ are not similar to those for $a = b$. As k becomes large, however, these differences diminish; the waiting times can then be reasonably approximated by a gamma distribution, calculated for the effective jump rate λ .

4. Distribution of Displacements

With the probability density $p_N(t)$ for the number of jumps during an interval t in hand, we can now write out the probability density for x . Using Eqs. (75)-(77) as well as (86) and (87), we find that for starts at an even site,

$$p_x = \sqrt{\frac{\pi(a-b)t}{2}} \exp[-(a+b)t] \sum_N \frac{(4ab)^{N/2} N!}{\left(\frac{N}{2}\right)! \left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)!} \\ \times \frac{t^{N/2}}{2^N [2(a-b)]^{N/2}} \{ I_{(N-1)/2}[(a-b)t] - I_{(N+1)/2}[(a-b)t] \} \\ x, N \text{ even} \quad (99)$$

$$p_x = \sqrt{\frac{\pi a}{b}} \exp[-(a+b)t] \sum_N \frac{(4ab)^{N/2} N!}{\left(\frac{N-1}{2}\right)! \left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)!} \frac{t^{N/2}}{2^{N[2(a-b)]^{N/2}}} I_{N/2}[(a-b)t]$$

x, N odd

If the initial position is an odd site, x on the rhs of Eq. (99) is replaced by $x-1$, and the rate constants a and b are interchanged.

In the limit $a=b$, it follows immediately from Eqs. (88) and (99) that

$$p_x = \exp(-2at) \sum_N (at)^N \left[\left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)! \right]^{-1} = \exp(-2at) I_x(2at). \quad (100)$$

That is, the probability density of x reduces to the form known⁶ to hold for an ordinary random walk continuous in time. It is of interest to compare this limiting density with that describing the actual displacement of dimers, according to Eq. (99). This is done in Fig. 10. The distributions clearly show two effects: 1) A gradual decrease in the probability of being at a point x as x increases. 2) Strong oscillations, caused by differences in jump rates from even and odd sites. It is clear that a Gaussian can be seriously in error as an approximation to any individual value of p_x . Averaging the probability over adjacent sites, however, reduces this problem. In Fig. 11, these averaged values are compared with a Gaussian, all at the same effective rate $\lambda = 2ab/(a+b)$. Even when the rates a and b are quite different, a Gaussian serves as a reasonable approximation to the averaged probability of finding a dimer in a specified unit cell.

V. SUMMARY

Elementary statistical techniques have been used to evaluate exactly the mean square displacement of small clusters, capable of existing in energetically different configurations at each site of the center of mass lattice. Two specific problems have been examined - the diffusion of dissociating dimers, and of bound trimers. The techniques used for the latter should also be adequate to describe the motion of larger clusters. However, the present development already suffices for the analysis of available experimental information, which will be presented separately.

The evaluation of the probability densities described here is more limited. Our approach is specific for dimers; examination of larger clusters will require new techniques. Even for such clusters, however, a crude estimate of the distance distribution should be possible by resorting to the averaging procedure found useful for dimers.

ACKNOWLEDGEMENT

Throughout this study we have had the benefit of stimulating discussions with Kaj Stolt about the behavior of clusters on surfaces.

APPENDIX: KOLMOGOROV'S EQUATION FOR $p_{x,i}$

If the primary concern is with the probability p_x that site x be occupied regardless of cluster configuration, then the formalism in Section I suffices. A more elaborate symbolism is required to evaluate the probability $p_{x,i}$ that a specified configuration i be at a given site. In general, rate constants for jumping from a site to its neighbor will depend both upon the initial and the final configuration of the cluster. We therefore denote the rate constant for transitions from x to $x+1$, starting in configuration h and ending in configuration i , by $\lambda_{x,hi}$; similarly the rate from x to $x-1$, starting in configuration h and ending in i is indicated by $\mu_{x,hi}$. The Kolmogorov equation for the probability $p_{x,i}$ of having a cluster at point x in configuration i , can now be written as

$$\begin{aligned} \frac{dp_{x,i}}{dt} = & \sum_h \lambda_{x-1,hi} p_{x-1,h} - \sum_h (\lambda_{x,ih} + \mu_{x,ih}) p_{x,i} \\ & + \sum_h \mu_{x+1,hi} p_{x+1,h} . \end{aligned} \quad (A1)$$

This relation is crucial to the discussion of trimer motion, for example. It is the basis of Eq. (45), for the probability of finding a trimer in configuration 1A.

In general, this detail is not necessary. We then regain a relation for the probability p_x of site x being occupied, regardless of the particular cluster configuration, by summing Eq. (A1) over all configurations i at x . That is,

$$\begin{aligned} \frac{dp_x}{dt} = \frac{d \sum_i p_{x,i}}{dt} = & \sum_{i,h} \lambda_{x-1,hi} p_{x-1,i} - \sum_{h,i} (\lambda_{x,ih} + \mu_{x,ih}) p_{x,i} \\ & + \sum_{h,i} \mu_{x+1,hi} p_{x+1,h} . \end{aligned} \quad (A2)$$

It is now useful to introduce the definitions

$$\begin{aligned}\lambda_{\mathbf{x}}^{\mathbf{p}} &\equiv \sum_{i,h} \lambda_{\mathbf{x},ih}^{\mathbf{p}} \\ \mu_{\mathbf{x}}^{\mathbf{p}} &\equiv \sum_{i,h} \mu_{\mathbf{x},ih}^{\mathbf{p}}\end{aligned}\quad (A3)$$

By the same steps sketched in Section I we obtain the differential equation for $\langle (\Delta \mathbf{x})^2 \rangle$:

$$\frac{d\langle (\Delta \mathbf{x})^2 \rangle}{dt} = 2[\langle \mathbf{x} \lambda_{\mathbf{x}} \rangle - \langle \mathbf{x} \mu_{\mathbf{x}} \rangle - \langle \mathbf{x} \rangle (\langle \lambda_{\mathbf{x}} \rangle - \langle \mu_{\mathbf{x}} \rangle)] + (\langle \lambda_{\mathbf{x}} \rangle + \langle \mu_{\mathbf{x}} \rangle). \quad (A4)$$

However, a more elaborate convention for the different symbols must now be recognized:

$$\begin{aligned}\langle \lambda_{\mathbf{x}} \rangle &= \sum_{\mathbf{x}} \sum_{i,h} \lambda_{\mathbf{x},ih}^{\mathbf{p}} & \langle \mu_{\mathbf{x}} \rangle &= \sum_{\mathbf{x}} \sum_{i,h} \mu_{\mathbf{x},ih}^{\mathbf{p}} \\ \langle \mathbf{x} \lambda_{\mathbf{x}} \rangle &= \sum_{\mathbf{x}} \sum_{i,h} \lambda_{\mathbf{x},ih}^{\mathbf{p}} \mathbf{x} & \langle \mathbf{x} \mu_{\mathbf{x}} \rangle &= \sum_{\mathbf{x}} \mathbf{x} \sum_{i,h} \mu_{\mathbf{x},ih}^{\mathbf{p}}\end{aligned}\quad (A5)$$

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¹For a review of observations on individual atoms, see G. Ehrlich, Surf Sci., In press.

²D. A. Reed and G. Ehrlich, J. Chem. Phys. 64, 4616 (1976). This paper will also be referred to as I.

³K. Stolt, W. R. Graham, and G. Ehrlich, J. Chem. Phys. 65, 3206 (1976).

⁴It should be noted, however, that on planes on which sites in adjacent diffusion channels are staggered with respect to each other, as for example on the (311) of the fcc lattice, three rate constants suffice for a rigorous account of trimer motion.

⁵G. Ehrlich, J. Chem. Phys. 44, 1050 (1966).

⁶P. A. P. Moran, An Introduction to Probability Theory (Clarendon Press, Oxford, 1968).

⁷The variance of x is identical with the mean square displacement in units of l/m , and the two terms will be used interchangeably.

⁸A solution for dimers existing in three states has recently been reported by U. Landman, E. W. Montroll, and M. F. Shlesinger, Phys. Rev. Lett. 38, 285 (1977).

⁹Present notation differs somewhat from that of I, in that A or B configurations are now noted in the subscript; previously they were indicated by separate superscripts.

¹⁰Note that the convention throughout is to start in the unit cell based on $x = 0$.

¹¹Handbook of Mathematical Functions, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D. C., 1964).

¹²The general approach followed here is similar to that used in the original derivations of the probability density for a randomized random walk. See reference 5, and also W. Feller, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. 14, 864 (1966).

¹³In the terminology of stochastic analysis, this problem corresponds to a pure birth process.

¹⁴Tables of Integral Transforms, edited by A. Erdélyi, W. Magnus, F. Oberhettinger, F. G. Tricomi (McGraw-Hill, New York, 1954) Vol. I.

FIGURE CAPTIONS

- Fig. 1. Schematic of dimer and trimer configurations in one-dimensional diffusion on a lattice represented by shaded circles. Open circles indicate clusters. Surface sites in adjacent channels are throughout assumed to be exactly abreast of each other. Spacing in close-packed direction is ℓ .
- Fig. 2. Rate constants for interconversion of dimer configurations on a one-dimensional lattice. Configurations are labelled by the separation between atoms, in units of ℓ , along the direction of diffusion.
- Fig. 3. Configurations allowed on the points x of the center of mass lattice of a dimer. Arrows indicate the jumps and jump rates between configurations on neighboring sites.
- Fig. 4. Schematic of potential energy relations for a dissociating dimer. Shading indicates separation at which interactions between adatoms in cluster vanish. $\Delta E_{\alpha}^{\ddagger}$ denotes diffusion barrier for a single atom.
- Fig. 5. Mean-square displacement of dissociating dimers, modeled on the behavior of Re on W(211).³ Parameters entering estimates are $\alpha_0 = 2.2 \times 10^{12} \exp(-17,500/RT)$, $\beta_1 = 2.5 \times 10^{12} \exp(-18,300/RT)$, $\alpha = 2.95 \times 10^{12} \exp(-19,800/RT)$, $P_s = 10.5 \exp(-E_2/RT)$, $P_2/P_1 = \exp(-E_2/RT)$, $\alpha_1 = 2.95 \times 10^{12} \exp[-(19,800 + cE_2)/RT]$. All estimates at $T = 330^\circ\text{K}$. Different degrees of dissociation are obtained by varying E_2 between 0 and 5000 cal/mole.

- Fig. 6. Configurations and rate constants for trimer diffusion. Energetically different configurations on the same site x are distinguished by A and B.
- Fig. 7. Probability density for the total number of jumps N made by a dimer during the interval t . All estimates in this and subsequent figures are made for the same effective jump rate $\lambda = 2ab/(a+b)$, for dimers originating in even positions.
- Fig. 8. Probability density for the number of jumps, averaged over adjacent values of N .
- Fig. 9. Probability density for the time T_k at which the k^{th} jump of the dimer occurs.
- Fig. 10. Probability density for the displacement x of the center of mass for a dimer. Continuous curve shows probability density for Gaussian walk with same effective jump rate.
- Fig. 11. Probability density for x , averaged over adjacent values of x . Density for Gaussian walk is indicated by continuous curve.

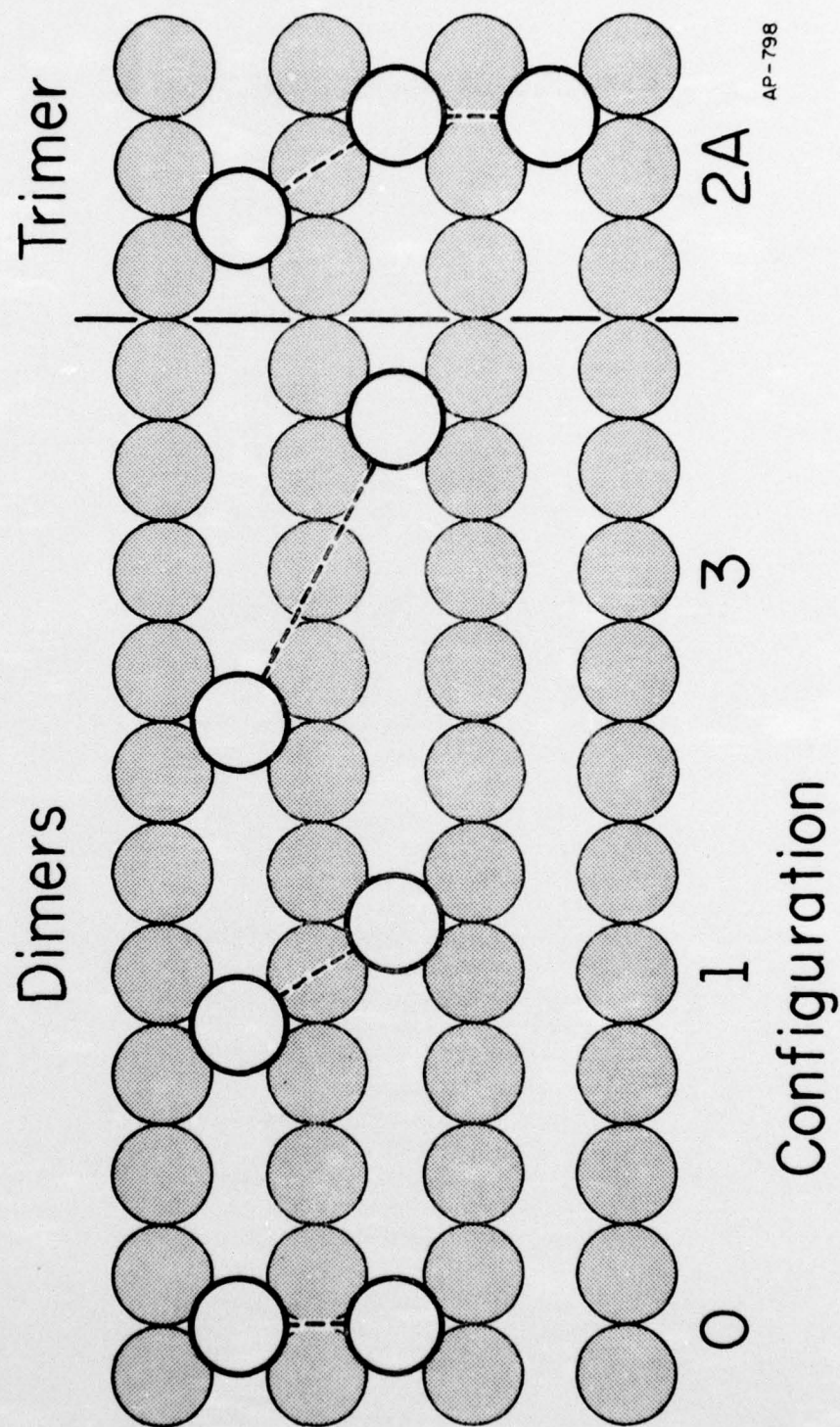
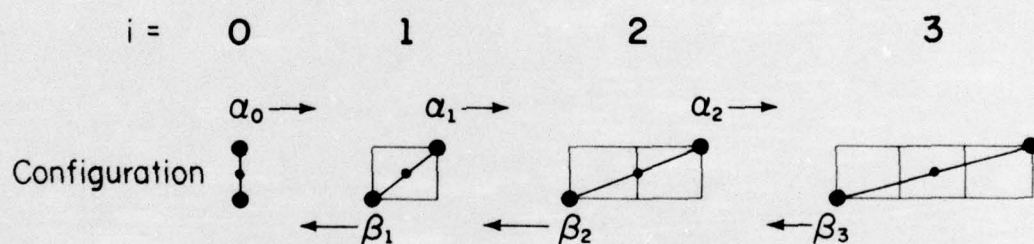


Fig. 1. Schematic of dimer and trimer configurations in one-dimensional diffusion on a lattice represented by shaded circles. Open circles indicate clusters. Surface sites in adjacent channels are throughout assumed to be exactly abreast of each other. Spacing in close-packed direction is ℓ .

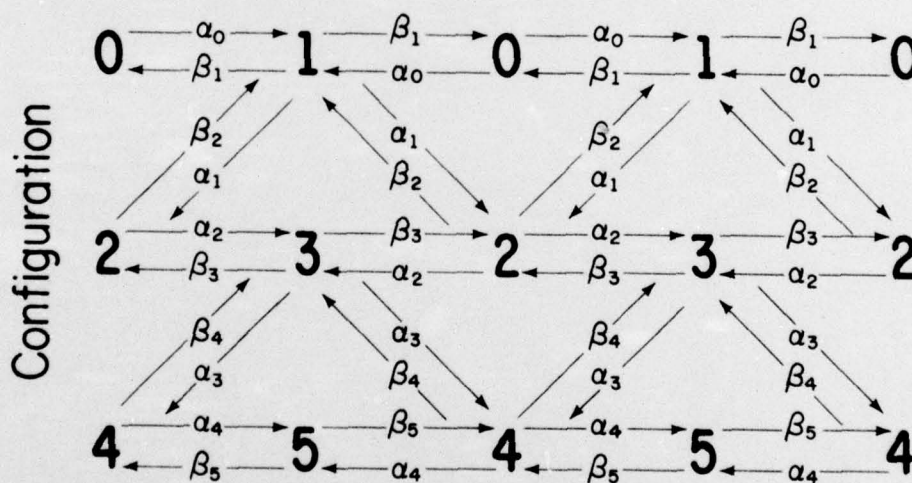


AP-795

Fig. 2. Rate constants for interconversion of dimer configurations on a one-dimensional lattice. Configurations are labelled by the separation between atoms, in units of l , along the direction of diffusion.

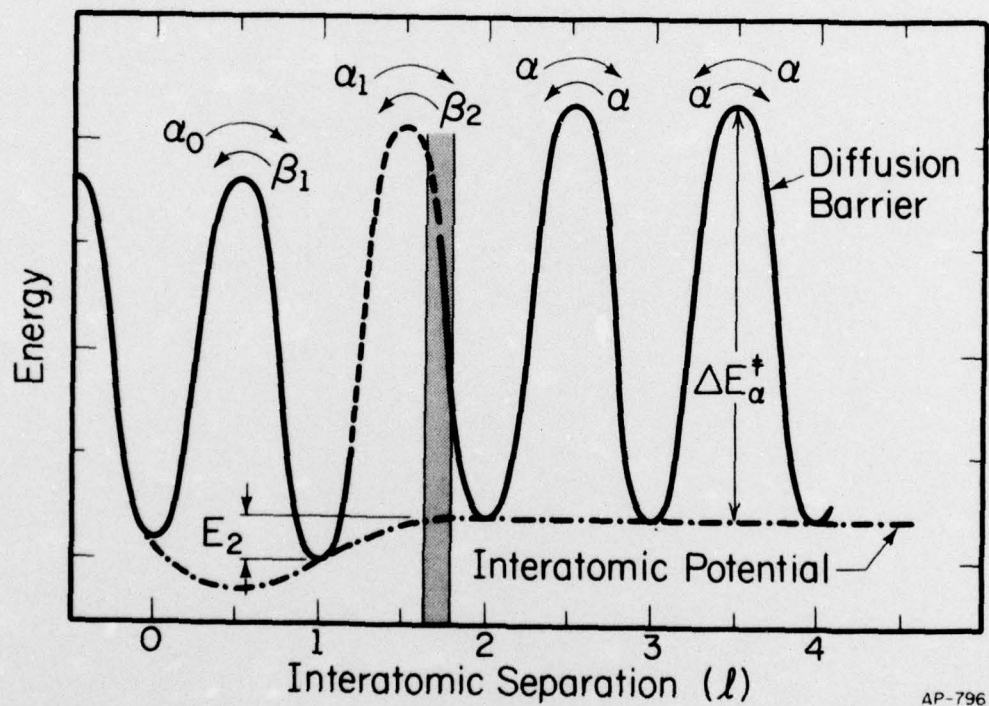
$$x =$$

-2	-1	0	1	2
+	+	+	+	+



AP-794

Fig. 3. Configurations allowed on the points x of the center of mass lattice of a dimer. Arrows indicate the jumps and jump rates between configurations on neighboring sites.



AP-796

Fig. 4. Schematic of potential energy relations for a dissociating dimer. Shading indicates separation at which interactions between adatoms in cluster vanish. $\Delta_{\alpha}^{\ddagger}$ denotes diffusion barrier for a single atom.

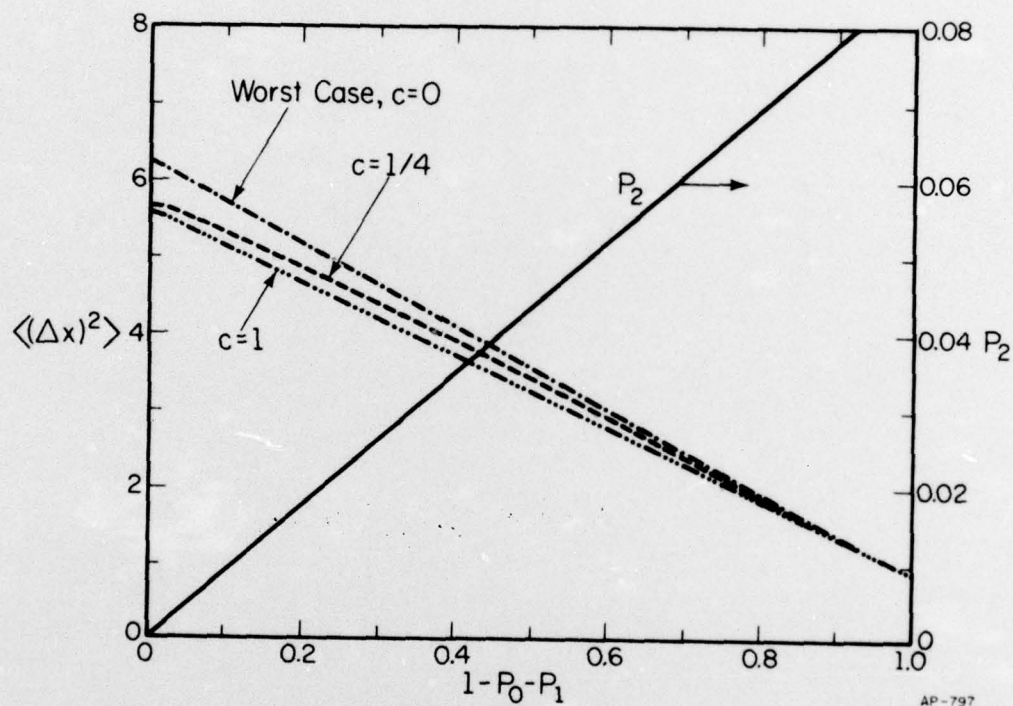
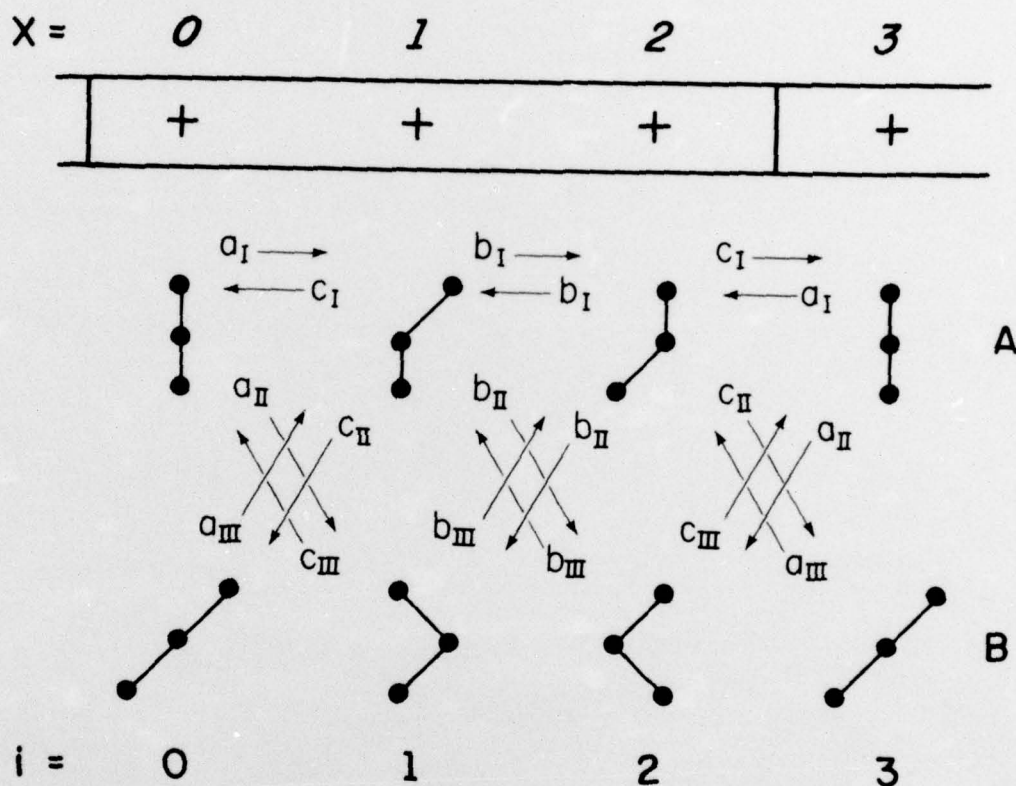


Fig. 5. Mean-square displacement of dissociating dimers, modeled on the behavior of Re on W(211).³ Parameters entering estimates are $\alpha_0 = 2.2 \times 10^{12} \exp(-17,500/RT)$, $\beta_1 = 2.5 \times 10^{12} \exp(-18,300/RT)$, $\alpha = 2.95 \times 10^{12} \exp(-19,800/RT)$, $P_s = 10.5 \exp(-E_2/RT)$, $P_2/P_1 = \exp(-E_2/RT)$, $\alpha_1 = 2.95 \times 10^{12} \exp[-(19,800 + cE_2)/RT]$. All estimates at $T = 330^\circ\text{K}$. Different degrees of dissociation are obtained by varying E_2 between 0 and 5000 cal/mole.



AP-797

Fig. 6. Configurations and rate constants for trimer diffusion. Energetically different configurations on the same site x are distinguished by A and B.

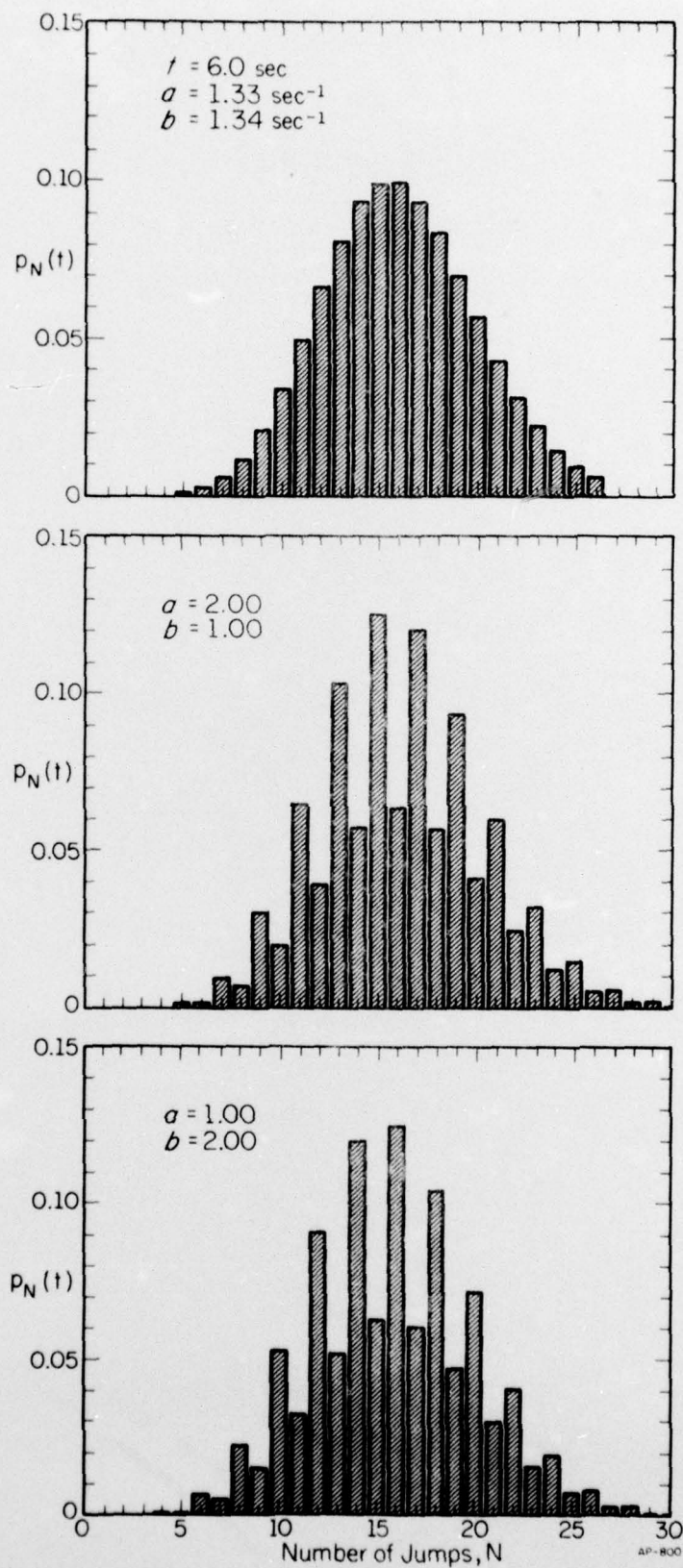


Fig. 7. Probability density for the total number of jumps N made by a dimer during the interval t . All estimates in this and subsequent figures are made for the same effective jump rate $\lambda = 2ab/(a+b)$, for dimers originating in even positions.

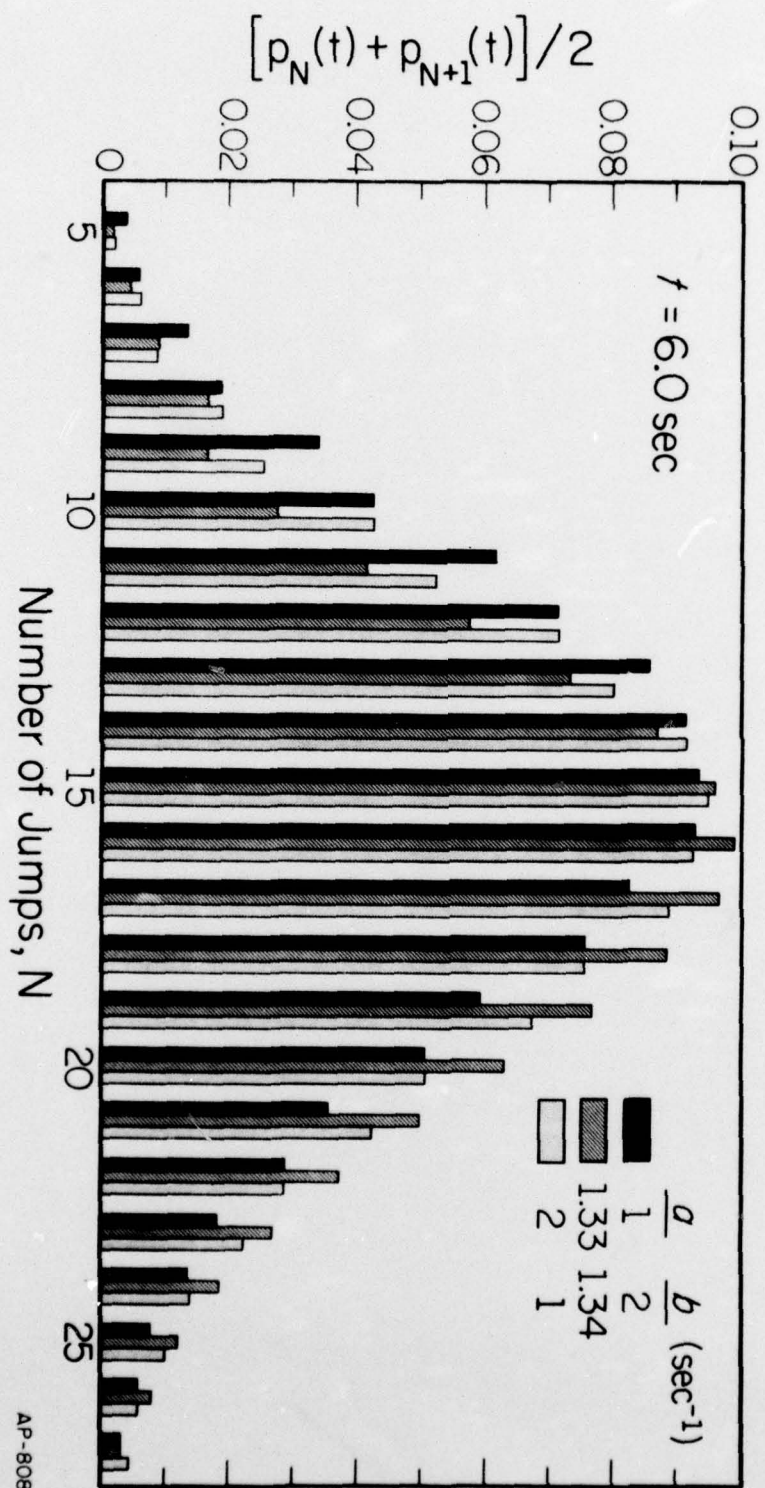


Fig. 8. Probability density for the number of jumps, averaged over adjacent values of N .

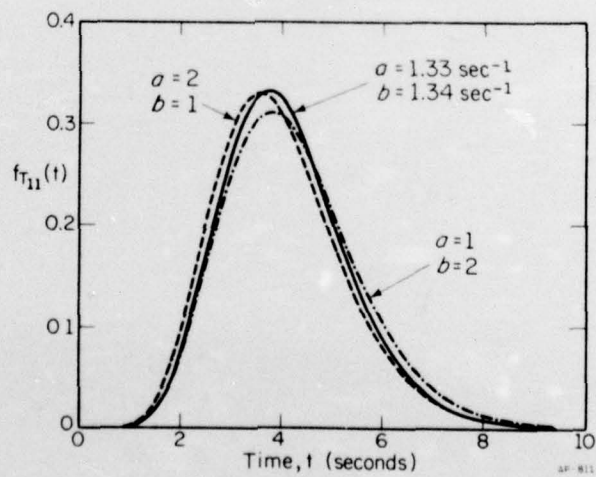
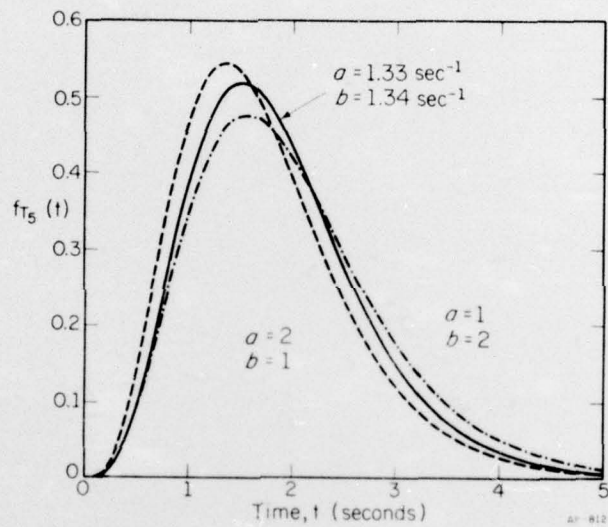
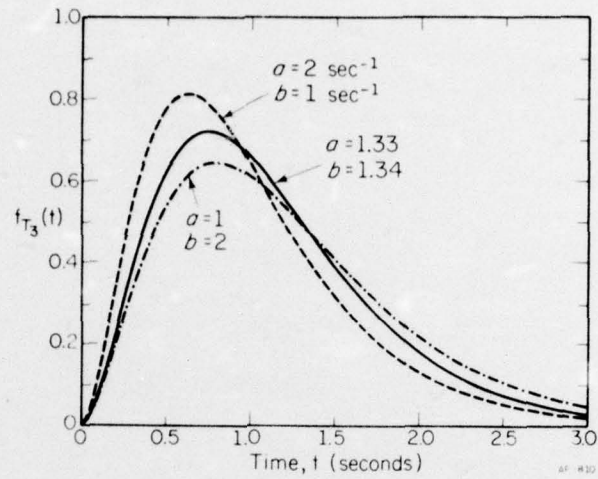


Fig. 9. Probability density for the time T_k at which the k^{th} jump of dimer occurs.

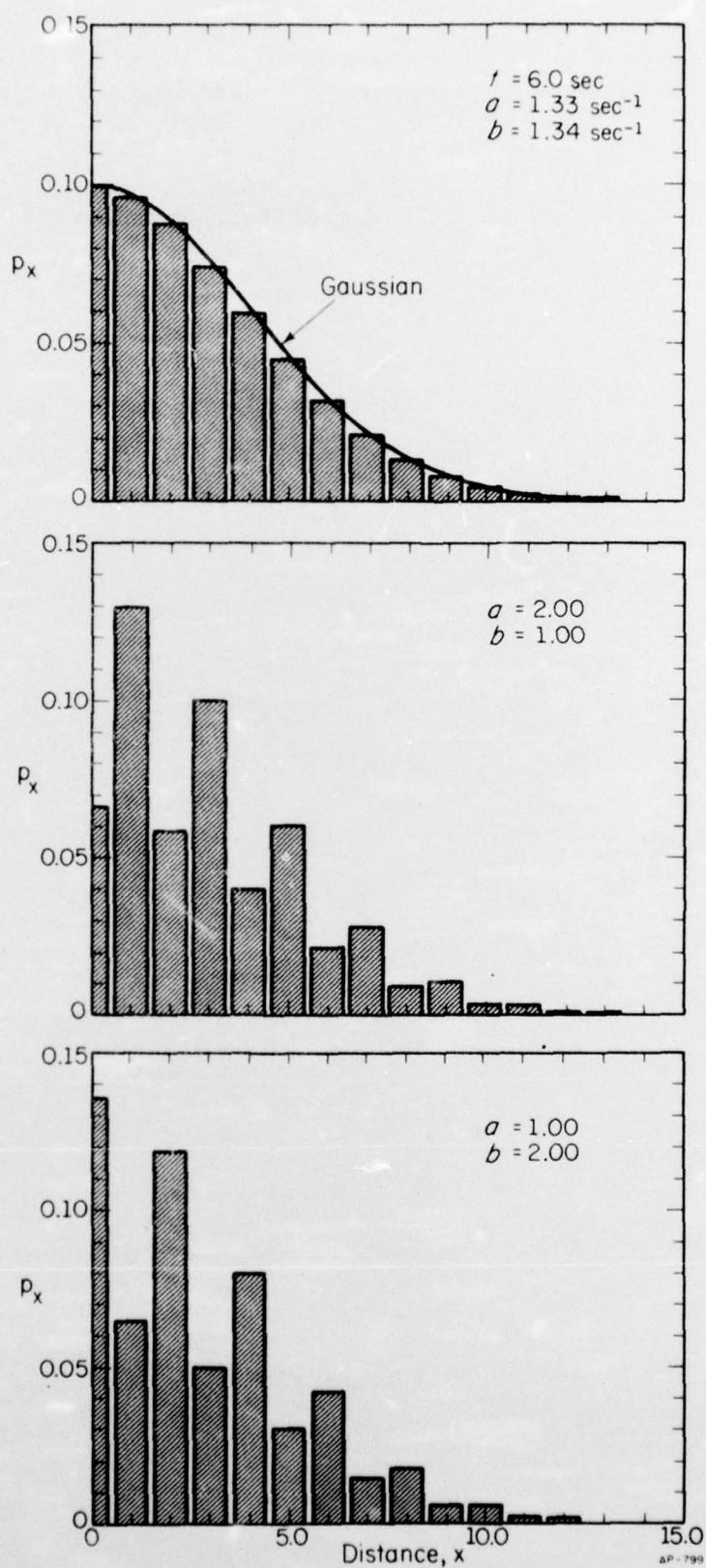


Fig. 10. Probability density for the displacement x of the center of mass for a dimer. Continuous curve shows probability density for Gaussian walk with same effective jump rate.

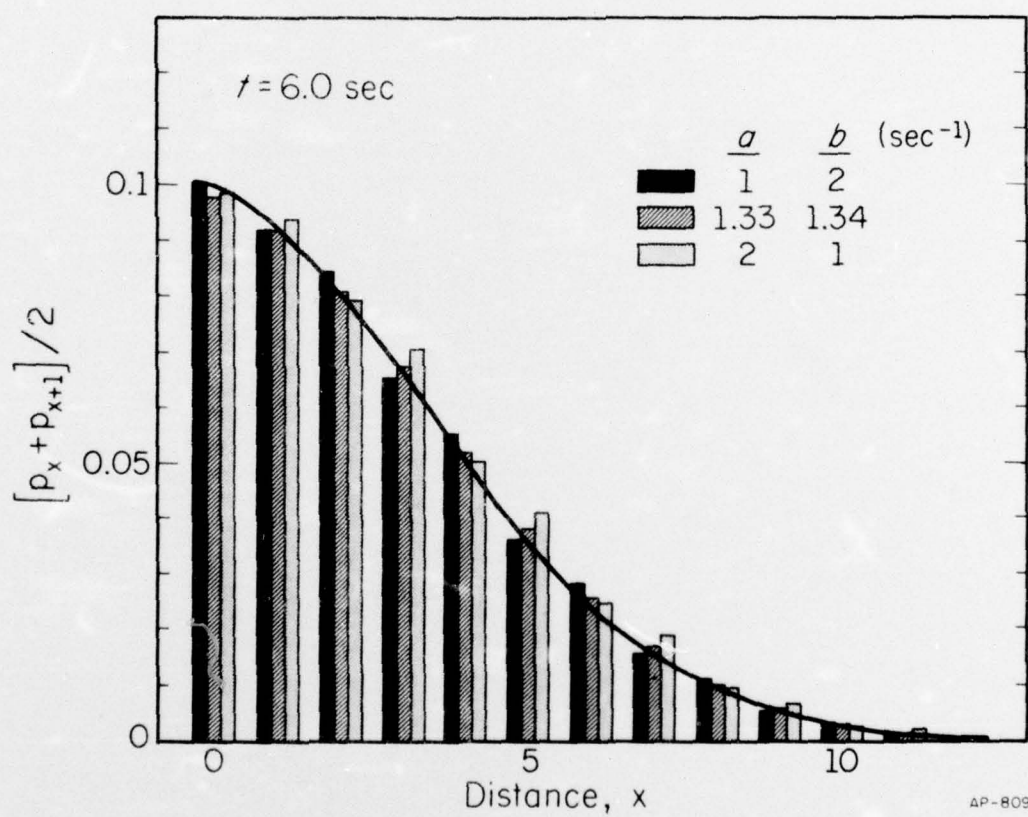


Fig. 11. Probability density for x , averaged over adjacent values of x . Density for Gaussian walk is indicated by continuous curve.